The Optimization of Diphenyl Methane Diisocynate Polymerization Process with the Used Frying Oil Polyalcohol to Foam Polyurethane Using RSM

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Abstract :

The used frying oil which was usually threw out and to be the waste had potency to be used as the material of polyurethane. Previously, it had to be converted into the polyol and then it was reacted with the Diphenyl Methane Diisocyanate (MDI). This research aimed to know the effect of MDI/polyol ratio and the quantity of the ethylene glycol on the compressive strength of polyurethane. The research was design by the Central Composite Design and the data was processed by the Response Surface Method. The calculation of data used the statistic 6. The choose variables as the independent variable were MDI/Polyol ratio (1, 2, and 3) and the quantity of ethylene glycol (10, 20, and 30 ml). The others were the fixed variable such as temperature (ambient), the quantity of catalyst (1 %) etc. The number of experiment which had to be done was 10 run. Based on the result of the data processing, the variable of MDI/Polyol ratio mostly affected the compressive strength of polyurethane. The optimal operation condition was achieved at MDI/Polyol ratio 1.82 and the quantity of ethylene glycol 25.177 ml. The produced polyurethane had the compressive strength 1,051.1 N/m^2.

Keywords: polyalcohol, polymerization, polyurethane, the used frying oil

1. Introduction

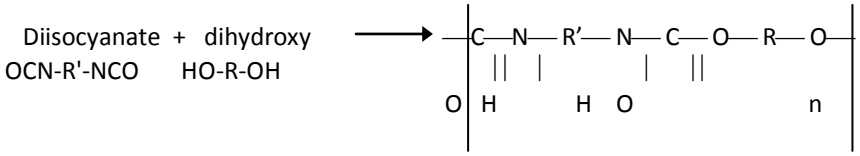
During this time polyurethane is usually manufactured from polyol and isocyanate produced commercially from the petroleum derivative product **[7]**. The petroleum is the non renewable resources and its reserve progressively attenuate so that it is necessary to be conducted the research to find out the alternative material. The materials that have potency to replace the petrochemical polyol are the vegetable oil such as canola oil, castor oil **[10]** , soybean oil **[13]**. The used frying oil that is derived from crude palm oil also has potency to be used as the polyurethane material.

The frying oil consumed in Indonesia is generally derived from CPO. CPO is the vegetable oil and the one of the renewable resources. Indonesia is recognized as the country producing CPO the biggest in the world. Indonesia produced 13.6 billion tons CPO in 2005 and about 6.328 billion tons is used to produce the frying oil (Refined Bleached Deodorized Oil) **[1]**.

The frying oil which has been used frequently cannot be utilized again because the content of free fatty acid (FFA) and peroxide compounds have increased. The frying oil is usually not permitted to be spent frequently more three times. Therefore the frying oil which has been used frequently more three times will be waste of the used frying oil. The dismissal of the used frying oil to the environment will disturb it clearly. The existence of the used frying oil waste will raise the BOD and COD so that many organisms will dead, generate the reek and stimulate the other environment problem.

This research activity had some goals i.e.: to process the polyol from the used frying oil to polyurethane, to know the trend of MDI/Polyol ratio and ethylene glycol effect on the polyurethane compressive strength and to get the composition which can generate the polyurethane with the high compressive strength.

Polyurethane is the polymer material made of dihydroxy and diisocyanate compounds by addition polymerization reaction. The general molecule structure of polyurethane derived from dihydroxy and diisocyanate compounds is as follows:



Polyurethane produced by the polymerization reaction really vary and complex. This complexity is caused by many variables which influence the final physic characters of polymer. They are i.e.:

1. The molecular weight and functionality of polyol and polyisocyanate.
2. The solubility properties of component and the result of reaction.
3. The using of many catalyst, surfactant, additive and filler can modify the physical properties and performance of polymer

The manipulation of these variables will generate polymers (PU) with different specification such as: thermoplastic elastomers, thermoset elastomers, engineering thermoplastics, rigid cellular plastics and felxible cellular plastics **[14]**.

Isocyanate usually used in the polyurethane manufacturing is 2 types, i.e.: aromatic and aliphatic isocyanate. Polyurethane made of aliphatic isocyanate has color more stable. However, it is less reactive than aromatic isocyanate and its price is more expensive. Therefore, almost 95 % polyurethane is produced by aromatic isocyanate, e.g.: Toluene Diisocynate (TDI), Diphenyl Methane Diisocyanate (MDI) and its derivate **[7]**. MDI is more favorable than TDI. The volatility of TDI is very high so that it causes some problems.

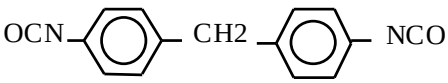


Figure 1.the molecule structure of 4,4 Diphenyl Methane Diisocyanate

Polyol is a polymer which has the molecular weight 250 – 8000 and the functionality of hydroxyl 1 – 8 (the number of hydroxyl is more 1). The important characteristics of polyol which concern with the its application in polyurethane are the functionality of hydroxyl and the distribution of hydroxyl group, the equivalent weight of hydroxyl, the composition of polymer chain and the structure of the hydroxyl group. Polyol which can be used in the manufacturing polyurethane are polyester polyol, polyether polyol and glyceride ploy ol which is from vegetable oil **[7]**.

Blowing agent is needed in the manufacturing of polyurethane foam to produce the bubbles of gas trapped in the polyurethane matrix. The chemical blowing agent is usually used in the manufacturing of flexible foam. The bubbles of gas CO_2 are generated from the reaction of blowing agent with isocynate, for examples: water and carboxylic acid. The physical blowing agent is generally utilized in the preparing of rigid foam. This type has the low bubble point so that it is easy to evaporate when it receives the heat of reaction, such as: trichlorofluoromethane, methylene chloride and so on.

Sometime the chain extender agent is added to modify the polyurethane properties. It usually utilized is difunctional compound such as glycol, diamine and hydroxyl-amine with low molecule weight.

2. Material and Methods

The materials utilized in the used frying oil polymerization process to polyurethane were the used frying oil hydrolyzed to polyalcohol, Diphenyl Methane Diisocyanate (MDI), ethylene glycol (EG) and methylene chloride. The used frying oil was obtained from the fried food seller in Semarang. MDI was bought from distributor. While ethylene glycol and methylene chloride each was bought at The Multi Kimia Raya (a chemical store in Semarang). The technical chemical can be used to synthesize polyol and polyurethane.

The main equipments spent in this experiment are as follows: polymerization reactor, stirrer, motor driving stirrer, thermo control, thermometer and mold. They were constructed as Figure 2.

The experiment was designed with central composite design method **[3]**. The variables choose as the independent variables were the MDI/the used frying oil polyol ratio and volume of ethylene glycol. The level value of the independent variables can be seen in Table 1. The others were the fixed variables such as, ambient temperature (30°C) dan total reactant mass volume (300 ml). The observed parameters/responses were the compressive strength of product and the molecule group in the structure of molecule. The quantity of experiment run which must be conducted was 10.

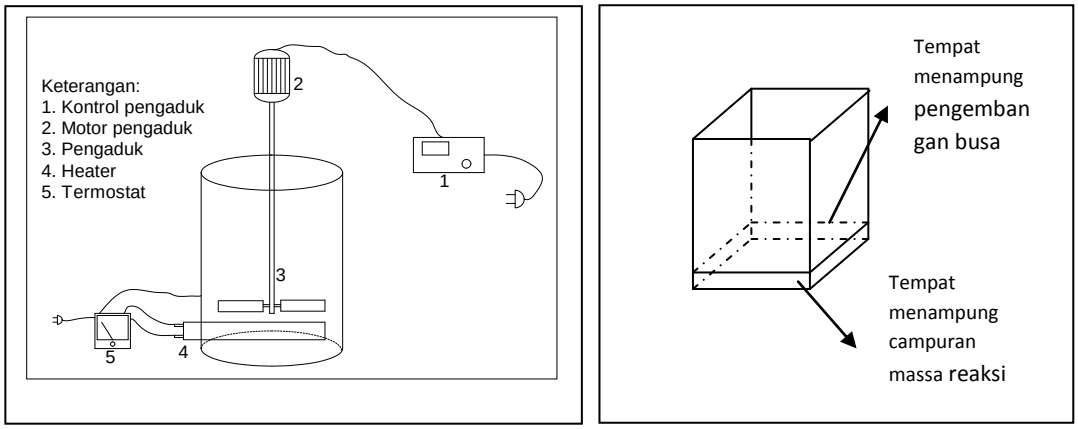


Figure 2.The construction of equipment and mold

Table 1. The variable of experiment

No	Variable	Low level	Center level	High level
1	Ratio of MDI/Polyol	1	2	3
2	Volume of ethylene glycol (ml)	10	20	30

3. Result and Discussion.

Previously the used frying oil utilized as the material must be characterized to know the properties. It has acid number 0.24, iodine number 68.22 and hydroxyl number 23.745. The iodine number 23.745 shows that the used frying oil has had the hydroxyl group. The hydroxyl group in the molecule is caused by the oxidation process during the heating when the used frying oil is utilized to fry the food. The iodine number 68.22 shows that the used frying oil still has the double bond more enough although it has undergone the heating process. Polyol produced from the used frying oil has the hydroxyl number 35 and iodine number/iodine value 19.

Table 2. Data of the compressive strength test of polyurethane (diameter of specimen 5 cm)

Run	MDI/Polyol Ratio	Ethylene glycol (ml)	Compressive force (N)	average (N)	Compressive sterngth (N/cm^2)
1	1	10	49.800	44.700	2.277,71
			39.600		
2	1	30	14.000	12.825	653,50
			11.650		
3	3	10	1.200	1.100	56,05
			1.000		
4	3	30	4.000	4.400	224,20
			4.800		
5	0,586	20	5.400	4.700	239,49
			4.000		
6	3,414	20	1.950	1.975	100,64
			2.000		
7	2	5,85	2.800	3.600	183,44
			4.400		
8	2	34,142	31.800	31.300	1.594,90
			30.800		
9	2	20	13.000	14.825	755,41
			16.650		
10	2	20	27.200	24.500	1.248,41
			21.800		

When the polymerization reaction occurred, temperature rose. It showed that the polymerization reaction of isocyanate and polyol was exothermic. The increasing of temperature of each run varied at range 80-135°C and initial temperature 30°C. Temperature was constant at few moment and then it gradually decrease at ambient temperature for 5 minute. When the reaction took place, it also occurred the forming of effervesce which will create the foam later. The produced polyurethane was characterized to know the compressive strength and the molecule structure. The result of the compressive strength test can be seen at Table 2. Data obtained from experiment is treated by Response Surface Method (RSM) to get the value of estimated effect, mathematic model equation, the comparison of observed and predicted polyurethane compressive strength and the optimal operation condition.

The value of estimated effect in Table 3 showed the effect of each variable to the polyurethane compressive strength. The linier and quadratic MDI/Polyol ratio variable had negative effect to the polyurethane compressive strength. While the linier and quadratic ethylene glycol volume variable had positive effect to the polyurethane compressive strength. The interaction variable of MDI/Polyol ratio and ethylene glycol volume also had positive effect to the polyurethane compressive strength. The estimated effect value of linier and quadratic MDI/Polyol ratio variable, ethylene glycol volume variable and the interaction variable are significant enough.

Tabel 3. The value of estimated effect and regression coefficient.

No		Effect	Regression Coefficient
1	Mean/Interc.	1001,910	1001,910
2	(1)MDI/Polyol Ratio(L)	-711,831	-355,915
3	MDI/Polyol Ratio(Q)	-695,221	-347,611
4	(2)Volume EG (ml)(L)	135,011	67,506
5	Volume EG (ml)(Q)	23,884	11,942
6	1L by 2L	896,180	448,090

The regression coefficient value included in table 3 was used to form the mathematic model equation which presents the relation of the polyurethane compressive strength with MDI/Polyol ratio variable and ethylene glycol volume variable. The mathematic model equation obtained is as follows:

$$Y = 1001{,}91 - 355{,}915\ x_1 + 67{,}506\ x_2 + 448{,}09\ x_1x_2 - 347{,}611\ x^2_1 + 11{,}942\ x^2_2$$

x_1 : Dimensionless variable of MDI/Polyol ratio
x_2 : Dimensionless variable of ethylene glycol volume.

The mathematic model equation can be spent to predict the polyurethane compressive strength at the given MDI/Polyol ratio and ethylene glycol volume. The comparison of observed and predicted polyurethane compressive strength is presented in Table 4.

The curve at 3 dimension optimization chart and surface contour chart has shape saddle/hyperbolic parabolic. It has the optimum point at saddle point (1.82; 25.177). Both charts show that the optimal polyurethane compressive strength will be achieved at MDI/Polyol ratio 1.82 and ethylene glycol volume 25.177 ml and the polyurethane produced has the compressive strength 1051.1 N/cm^2 (10.51 MPa).

Table 4. The comparison of observed and predicted polyurethane compressive strength.

Run	X_1	X_2	Y_o	Y_p	Residual/error
1	1.000	10.000	2277.710	1402.741	874.969
2	1.000	30.000	653.500	641.572	11.928
3	3.000	10.000	56.050	-205.270	261.320
4	3.000	30.000	224.200	825.922	-601.722
5	0.586	20.000	239.490	810.029	-570.539
6	3.414	20.000	100.640	-196.652	297.292
7	2.000	5.858	183.440	930.326	-746.886
8	2.000	34.142	1594.900	1121.261	473.639
9	2.000	20.000	755.410	1001.910	-246.500
10	2.000	20.000	1248.410	1001.910	246.500

Note
X_1 : MDI/Polyol ratio variable ; X_2 : Ethylene glycol volume variable (ml) ; Y_o : Observed polyurethane compressive strength ; Y_p : Predicted polyurethane compressive strength with mathematic model.

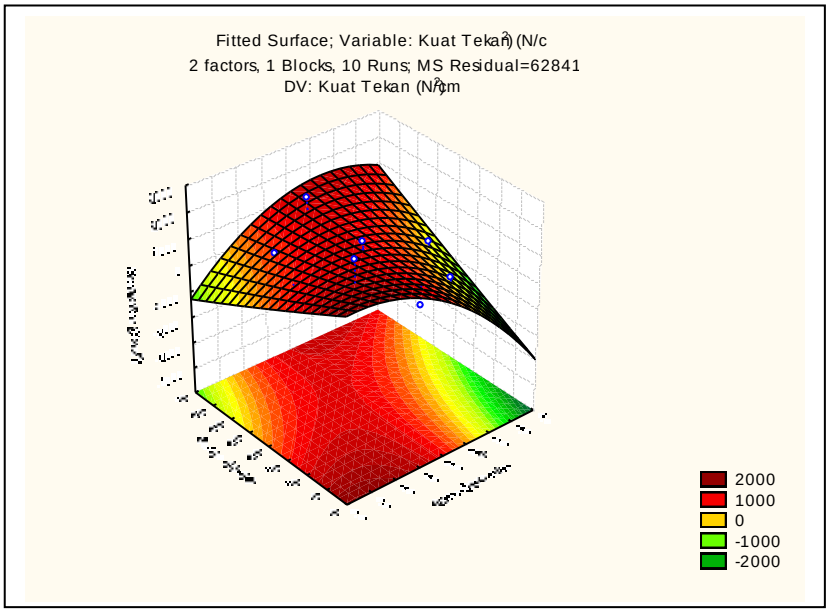


Figure 3. The 3D optimization chart (the compressive strength (N/cm^2) vs MDI/Polyol ratio and EG volume (ml)

The rigid polyurethane foam made of canola oil had the compressive strength 770 ± 145 kPa. While the rigid polyurethane foam manufacture from castor oil had the compressive strength 415 ±50 kPa (Suresh S. et al, 2007). Rigid polyurethane foam resulted of the used frying oil has the compressive strength 10.51 MPa. Rigid PU foam from the used frying oil has more compressive strength than rigid PU from canola and castor oil.

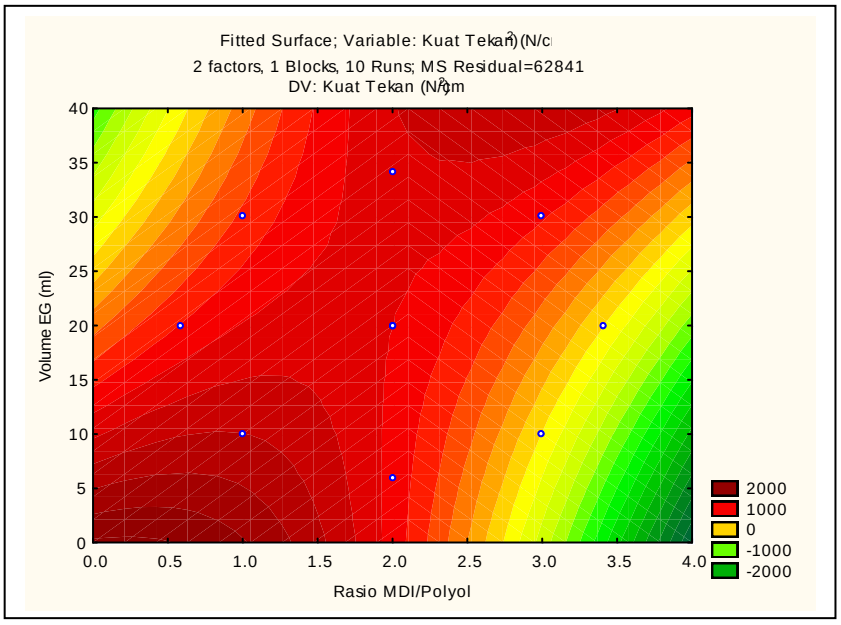


Figure 4.Surface contour chart of the compressive strength (N/cm^2) vs MDI/Polyol ratio and EG volume (ml)

The FTIR spectra of polyurethane from the used frying oil is presented in figure 5 and the FTIR spectra of polyurethane from canola oil, soybean oil and castor oil are shown in figure 6. The existence of urethane group can be showed with the absorption of stretching vibration N – H at frequency 3125 - 3570 cm^{-1}, the absorption of bending vibration N – H at frequency 1550 – 1510 cm^{-1}, the absorption of stretching vibration C=O at frequency 1740 – 1690 cm^{-1} and the absorption of stretching vibration C – N at frequency 1400 cm^{-1}.

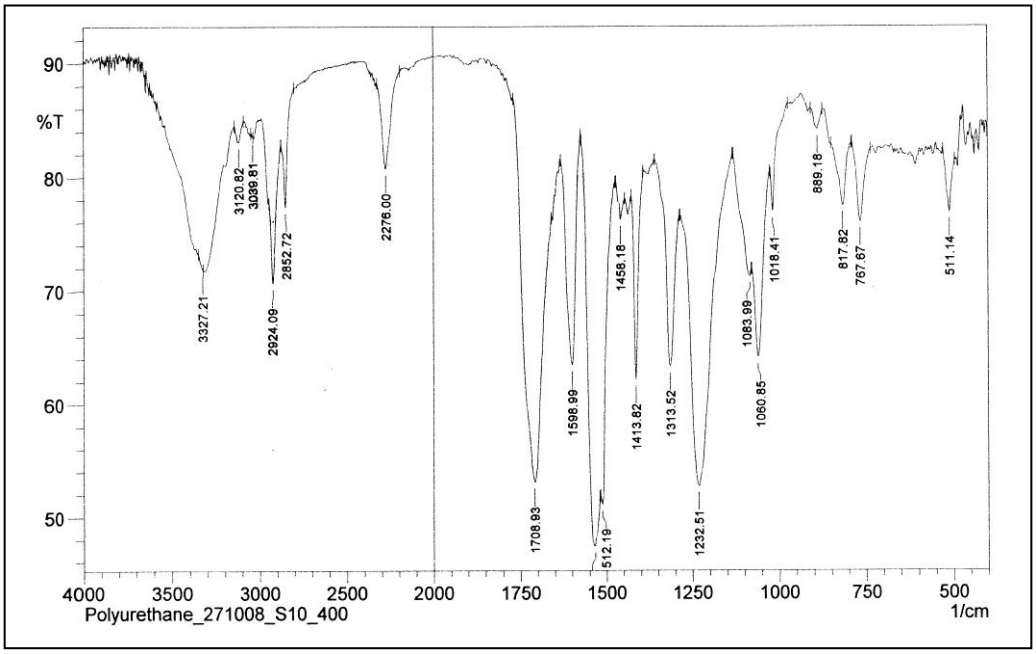


Figure 5. FTIR spectra of Polyurethane generated from the used frying oil.

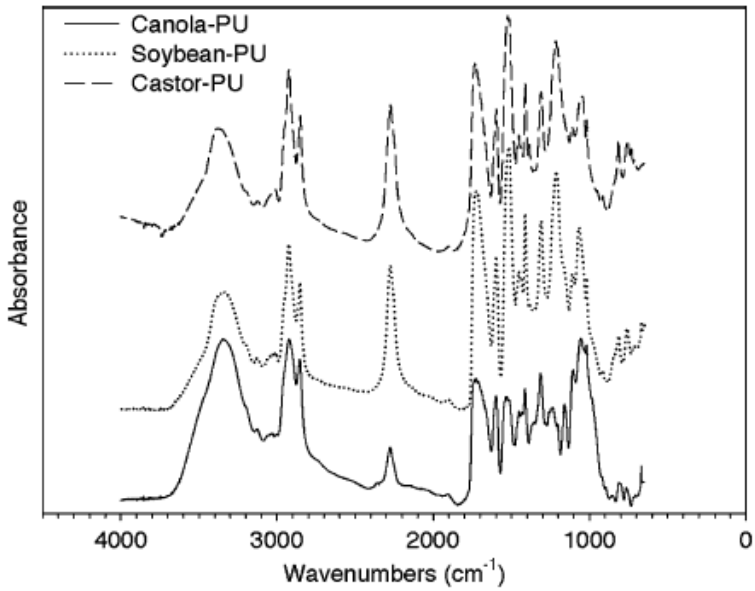


Figure 6. FTIR spectra of Polyurethane from canola oil, soybean oil and castor oil **[10]**.

4. Conclusion

1. The value of estimated effect shows that all variable mostly affect to the polyurethane compressive strength.
2. MDI/Polyol ratio variable and ethylene glycol volume variable cannot be interpreted individually.
3. The optimal operation condition of producing polyurethane is achieved at MDI/Polyol ratio 1.82 and ethylene glycol volume 25.177 ml.
4. The resulted polyurethane has the compressive strength 1051.1 N/cm^2 (10.51 MPa).

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